SUNWAY UNIVERSITY

Snap frozen metastable polymorphs – a story of a tetra-morphic one-dimensional coordination polymer

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Research Centre for Crystalline Materials

The 45th Congress on Science and Technology of Thailand (STT45)

Overview

MOF's for sustainable development

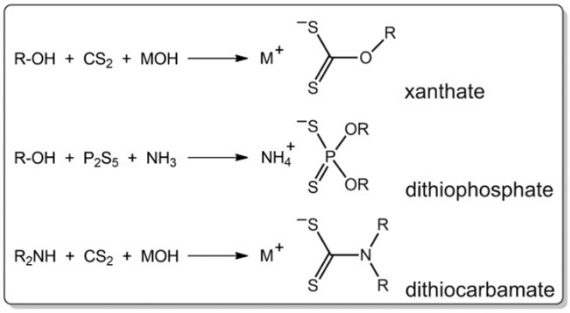
1,1-dithiolate ligands

Zinc-triad elements:
Homoleptic compounds

Complexation with bipyridyl-bridges

Snap frozen!

Synthesis



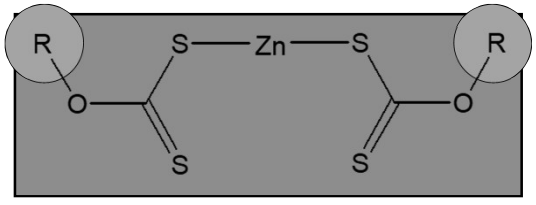
Metathesis: $AX_2 + 2\ MS_2COR \longrightarrow A(S_2COR)_2 + 2MX$

Zinc thiolates: tuning supramolecular aggregation

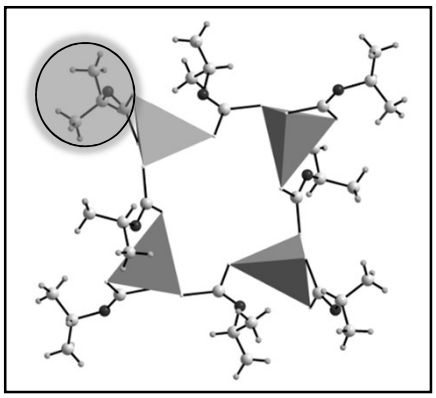
Molecular paving with zinc xanthates

Tailoring luminescence

Structural diversity in $Zn(S_2COR)_2$



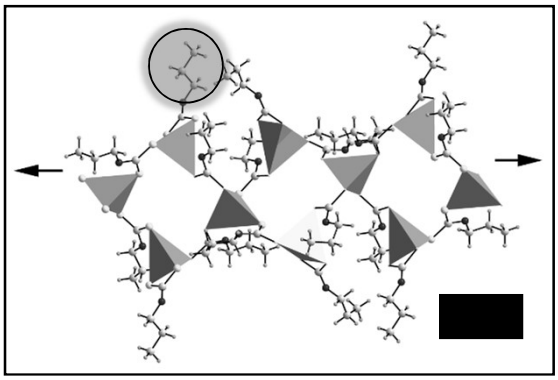
Examine structures for which R = Et, nPr & iPr



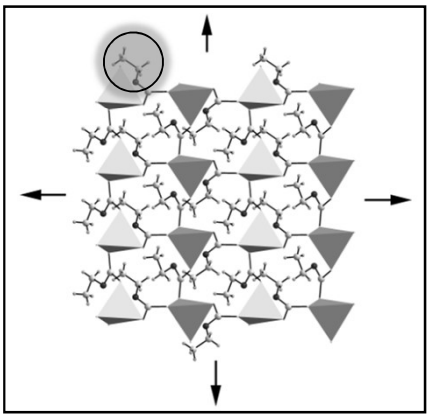
R = iPr

[redacted]

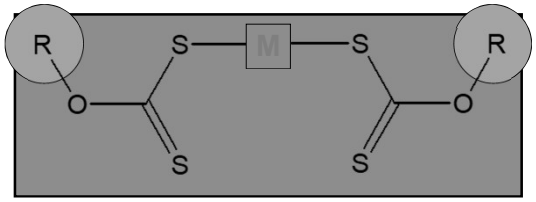
R = nPr



R = Et

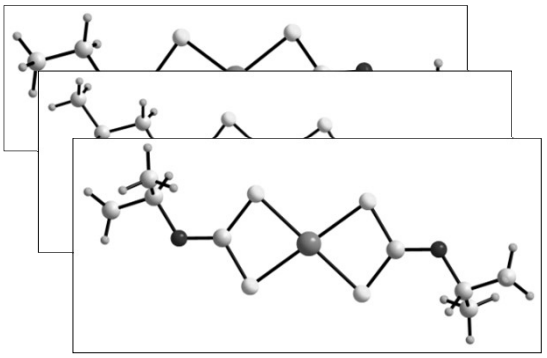


Structural diversity in $M(S_2COR)_2$

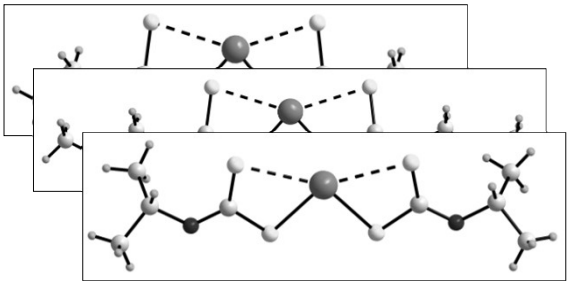


Examine other structures for which
M = Ni(II) & Te(II); R = Et, nPr & iPr

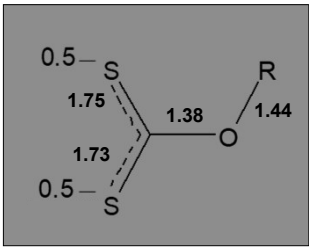
$Ni(S_2COR)_2$ for R = Et, nPr & iPr



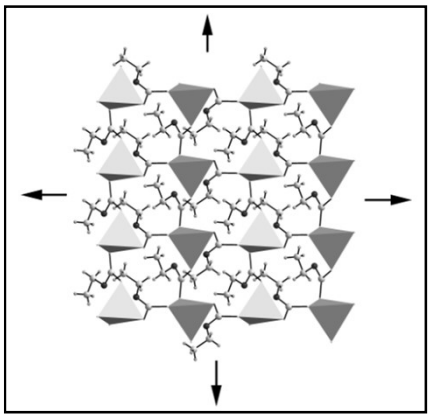
$Te(S_2COR)_2$ for R = Et, nPr & iPr



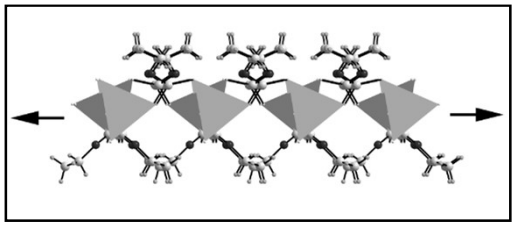
Ab initio molecular orbital calculations
on $^{-}S_2COR$

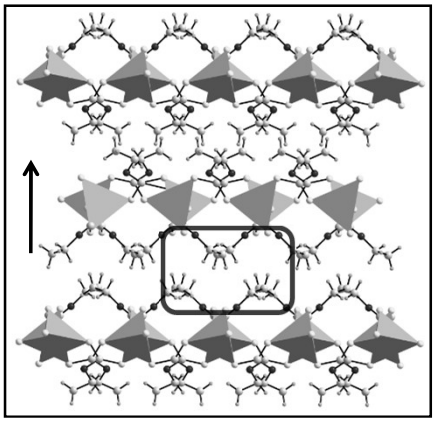


R = Et

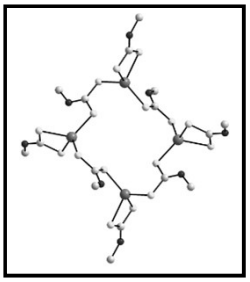


Molecular paving with $Zn(S_2COEt)_2$





Molecular paving with $Zn(S_2COR)_2$



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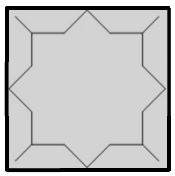
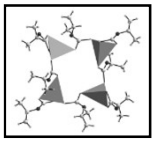
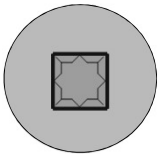


'molecular paving stone'

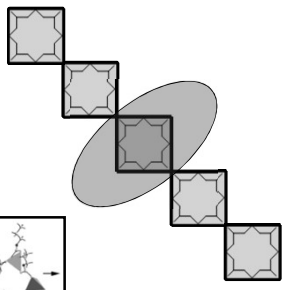
Molecular paving with $Zn(S_2COiPr)_2$

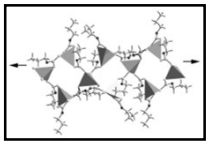




3-D exclusion zone

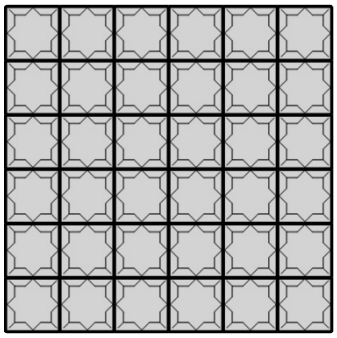
Molecular paving with $Zn(S_2COnPr)_2$





2-D exclusion zone

Molecular paving with $Zn(S_2COEt)_2$



Conclusions #1

Systematic analyses are vital

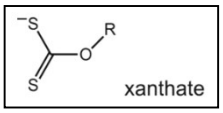
A new design element in crystal engineering

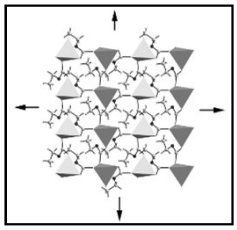
Au···Au

Coordination polymers of zinc-triad elements

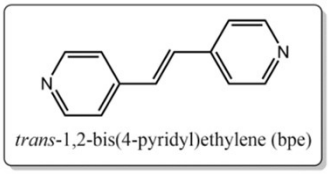
Solid-state polymers cf. solution

$Zn(S_2COR)_2$ + bridging ligands

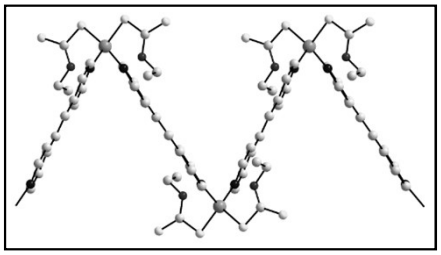




Zinc(1,1-dithiolate)$_2$ + bpe

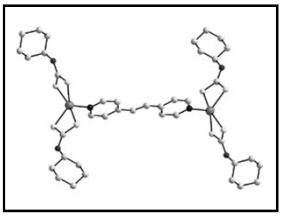


Zinc(xanthate)$_2$ + bpe



R = Et

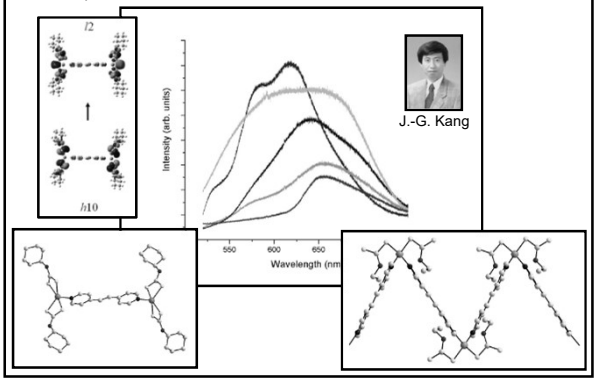
Zinc(xanthate)$_2$ + bpe



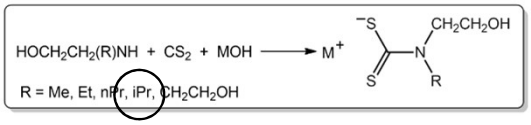
R = Cy

Steric bulk!

Implications for solid-state luminescence



Introducing hydrogen-bond functionality into dithiocarbamate ligands



Au···Au

Cadmium dithiocarbamates: $\{Cd[S_2CN(iPr)CH_2CH_2OH]_2.solvent\}_n$

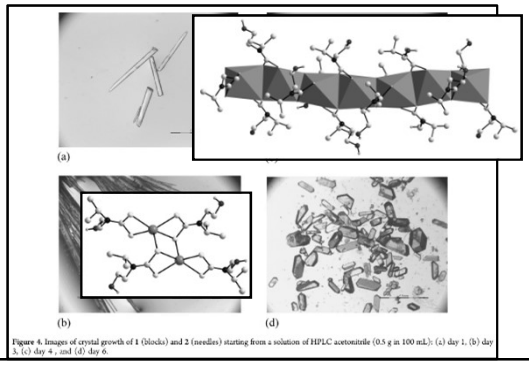
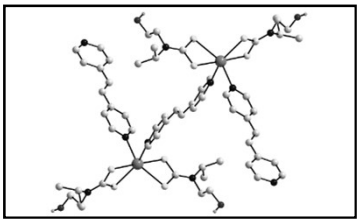


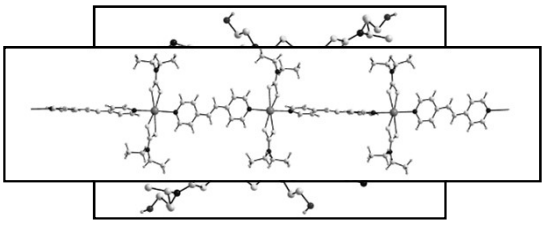
Figure 4. Images of crystal growth of 1 (blocks) and 2 (needles) starting from a solution of HPLC acetonitrile (0.5 g in 100 mL): (a) day 1, (b) day 3, (c) day 4 , and (d) day 6.

Cadmium dithiocarbamates: $\{Cd[S_2CN(iPr)CH_2CH_2OH]_2\}_n$ + bpe



Product regardless of the ratio of reagents
2:1, 1:1 and 1:2

Cadmium dithiocarbamates: $\{Cd[S_2CN(iPr)CH_2CH_2OH]_2\}_n$ + bpe



Product regardless of the ratio of reagents
2:1, 1:1 and 1:2

Conclusions #2

See Conclusions #1

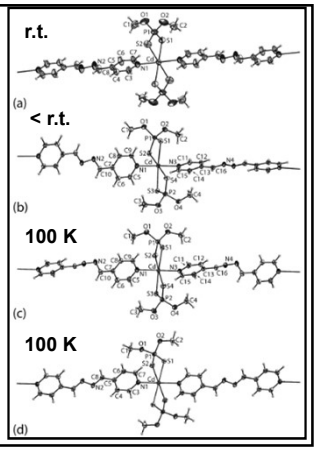
A competition between coordinate bonds and hydrogen bonding?

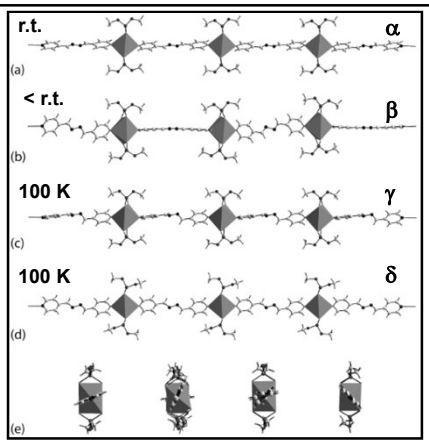
Au···Au

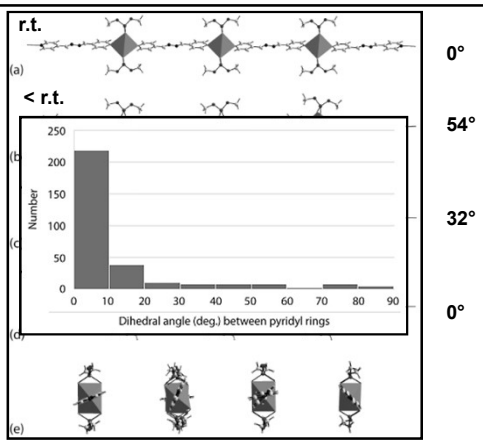
Cadmium dithiophosphates:

$\{Cd[S_2P(OMe)_2]_2$-4-PyAld$\}_n$

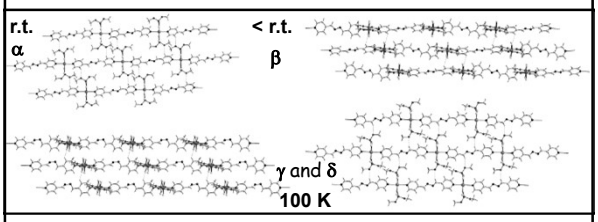
Tan Yee Seng







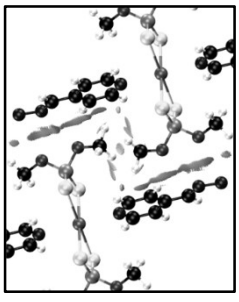
Unit cells: Stacking of layers



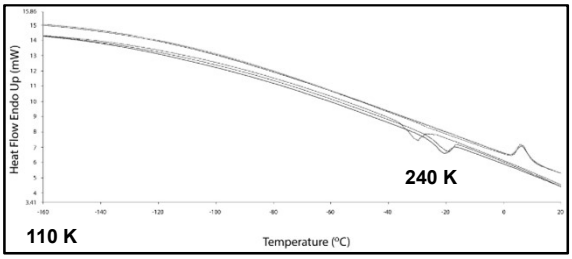
Alberto Otero-de-la-Roza

Lattice Energies

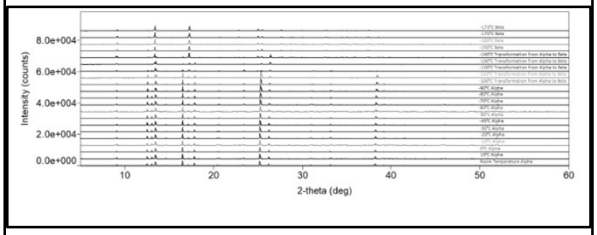
r.t.	α	0 kcal/mol
< r.t.	β	1.52
100 K	γ	2.62
100 K	δ	1.97



Inter-conversion – bulk material: DSC



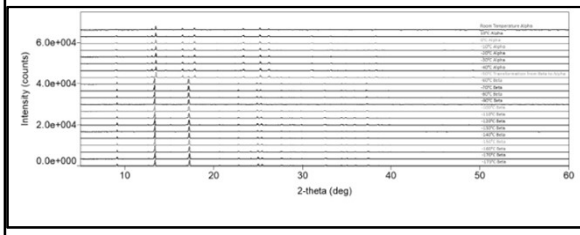
Inter-conversion – bulk material: PXRD



Cooling cycle – r.t. to < r.t.

[redacted]

Inter-conversion – bulk material: PXRD



Heating cycle – < r.t. to r.t.

[redacted]

Inter-conversion – single crystals

263 - 223 K

α → β → [redacted]

cooling

100 K		r.t.	
268 – 293	β	α	1.52 kcal/mol
120 – 130 γ	β	α	2.62
140 – 150 δ	β	α	1.97

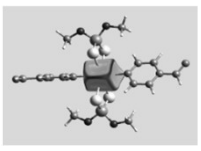
[redacted] heating

Hirshfeld surfaces for metal centres

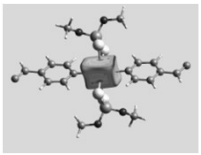
The trans-N_2S_4 donor sets are not the same:

Cd / S_2P plane

0.357(2) 0.2816(12) 0.1906(16) 0.8665(17)



Mukesh Jotani



Conclusions #3

One-off, 100 K experiments need supporting data

Au···Au

Fortuna Eruditis Favet ("*Fortune favours the prepared mind*")